

the surface inwards into the crystalline sulphate. Further, barium sulphate is known to occur as a pseudomorph of barytocalcite.

The abundant presence of calcium sulphate in the sandstone in the neighbourhood of Nottingham points to the probability of the barium sulphate having been formed *in situ* by the process of double decomposition, and probably from barium carbonate which has been found elsewhere in sandstone beds of the same formation.

XV. "Deposits of Barium Sulphate from Mine-water." By FRANK CLOWES, D.Sc., Principal and Professor of Chemistry and Metallurgy in University College, Nottingham. Communicated by Professor ARMSTRONG, F.R.S. Received June 6, 1889.

Specimens of remarkable deposits which have formed in the water-boxes of coal-mines in the neighbourhood of Newcastle-upon-Tyne have been for many years in the possession of the Museum of the Durham College of Science.

A rough analysis has been published by J. T. Dunn ('Transactions of the Newcastle Chemical Society,' vol. 3, p. 261) of an apparently similar deposit, which was formed during the autumn of 1876 in the Jane Pit at Walker. During this short period the sectional area of the box had been reduced by the deposit from seven and a half square inches to less than half a square inch, and had been in places almost completely closed. The deposit consisted of layers which were alternately white and brown, and was moderately soft. Analysis showed the percentage composition to be 90 of  $\text{BaSO}_4$ , 8 of  $\text{SrSO}_4$ , 1 of  $\text{CaSO}_4$ , the remainder consisting mainly of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ . The water passing through the box at the time of the examination contained no trace of barium or of strontium.

Another similar deposit was found by Dr. Richardson ('Brit. Assoc. Report,' 1863) to contain about 90 per cent. of barium sulphate and 3 of calcium sulphate, the remainder consisting of silica, alumina, ferric oxide, and moisture.

Professor Lebour states the pipes which convey water from the colliery workings of the Newcastle district are frequently entirely blocked in a short space of time with deposits, amongst which barium sulphate is seldom absent, and is often the chief constituent; and he draws attention to the fact that veins of barium sulphate are by no means uncommon in the coal measures of that district.

This deposition of barium sulphate is of interest in connexion with the discovery of the sulphate as a cementing material in sandstone near Nottingham, and as no complete analysis existed of the water-box deposits in the Durham College Museum, Professors

Bedson and Lebour have kindly furnished me with sections for chemical examination. The following results were yielded by the analyses:—

	Harton, box-deposit.	Jane Pit, Walker- deposit.	Newsham, box-deposit.
Loss at 100°.....	0·83	0·26	0·39
Loss by ignition.....	2·15	1·51	1·95
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .....	5·44	0·12	0·37
$\text{BaO}$ .....	56·72	61·30	61·09
$\text{SrO}$ .....	trace	0·35	0·09
$\text{CaO}$ .....	1·09	0·70	0·82
$\text{MgO}$ .....	0·12	0·14	trace
$\text{SO}_3$ .....	31·10	33·80	32·82
$\text{SiO}_3$ .....	1·19	0·53	0·22
Alkalies, &c. (by difference)	1·36	1·29	2·25
 $\text{BaSO}_4$ .....	86·37	93·35	93·03

The above deposits were mainly buff-coloured with thin layers of brown interposed; they were soft and loose, powder being easily detached by rubbing the surface with the finger. There was no appearance of crystallisation, but every indication of the deposit having been formed by rapid precipitation.

Professor Bedson ('Journ. Soc. Chem. Industry,' vol. 6, p. 712) and others have found barium chloride to be a common constituent of colliery waters of the district in which the above deposits have been formed. Relatively large quantities of the chloride have been found in some of these samples. The deposition may possibly arise from the admixture with such water of water containing sulphuric acid or ferrous sulphate, or both; since these substances are constantly formed by the oxidation of pyrites in the coal or in the associated shale beds. Or the barium sulphate occurring in veins in the coal measures may pass into solution under conditions yet unknown, and be deposited again as such.

Bischof mentions that hot springs may contain  $\text{BaCO}_3$  and  $\text{Na}_2\text{SO}_4$  together in solution; since at high temperatures these substances do not undergo double decomposition. Such a spring water will, however, deposit  $\text{BaSO}_4$  as it cools; since at ordinary atmospheric temperatures  $\text{BaSO}_4$  and  $\text{Na}_2\text{CO}_3$  are produced by the interchange of constituents. Possibly alteration of temperature may in a similar manner give rise to the above remarkable water-box and pipe deposits.

Possibly the deposition of barium sulphate in the form of stalactite, which has occurred in some parts of Derbyshire, may be due to the same causes as these mine-water incrustations.